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EFFECTS OF SURFACE PREPARATION TECHNIQUES ON THE ADHESION OF TANTALUM SPUTTERED COATINGS

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Oxalic acid brighteners are environmentally friendly and used commercially for metal and wood brightening, as well as for the removal of rust on household items (i.e., bathtubs, sinks, dishwashers). This study demonstrated that the prepared solution can be employed as a mild etchant for gun steel. Micro-scratch adhesion tests suggest that oxalic acid etching can improve the adhesion strength of a sputtered tantalum coating to steel. A potential advantage of this benign acid treatment would be the replacement of current electropolishing processes, which utilize acids (i.e., phosphoric, sulfuric, hydrochloric) to prepare the surface of gun steel prior to electro-plating. The use of these highly corrosive and toxic acids leads to high costs of hazardous material maintenance, cleanup, and disposal.

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INTRODUCTION

Prior to electroplating and sputtering deposition of a coating onto large caliber gun tubes, the gun steel surface must undergo metal cleaning procedures necessary for the coating to adequately adhere. Common procedures to prepare metals include electro-cleaning and electro-polishing. Current gun-tube electro-polishing processes use sulfuric and phosphoric acids for material removal and surface polishing prior to electroplating. Suitable replacements for these toxic materials and processes, which will eliminate costs incurred both environmentally and economically, are under investigation. One such process, which holds promise, is oxalic acid etching. Oxalic acid brighteners are environmentally friendly and used commercially for metal and wood brightening, as well as for the removal of rust on household items (i.e., bathtubs, sinks, dishwashers). In addition to their benign nature, there is also no need to apply a voltage, as in electro-polishing.

In this study, an oxalic acid based solution was used to clean the surface of several steel specimens prior to sputtering. The oxalic acid solution can remove steel at rates of up to 1½ mil/hr, which is comparable to the 1 mil/hr in current electro-polishing practices. Tantalum coatings were deposited via sputtering in the planar magnetron system. The coatings were sputtered onto small arc sections from a 120-mm gun tube that were prepared using four different surface preparation techniques:

1. Standard honing to a 16-µin. surface finish (specimens AH-1 and 2).
2. Oxalic acid etching (specimens OE-1 and 2).
3. Sulfuric/phosphoric electro-polish (specimens EP-1 and 2).
4. Fine polishing to a 2- to 4-µin. finish (specimens FP-1 and 2).

After the initial surface preparation (i.e., two sets of oxalic etching, polishing, etc.), the specimens were ultrasonically cleaned in acetone and alcohol and placed into a vacuum system. Each set of specimens was plasma cleaned in-situ for 30 minutes in Ar at a pressure of 5 mtorr, a current density of 3 mA/cm^2, and a voltage of 300 V to remove the native oxide prior to sputtering. Four specimens (one from each cleaning technique) were then sputtered simultaneously (Figure 1), making a total of eight specimens. This arrangement ensured that the deposition conditions were identical for each specimen and that each specimen had the same thickness. The surface finish of each specimen prior to sputtering is given in Table 1.

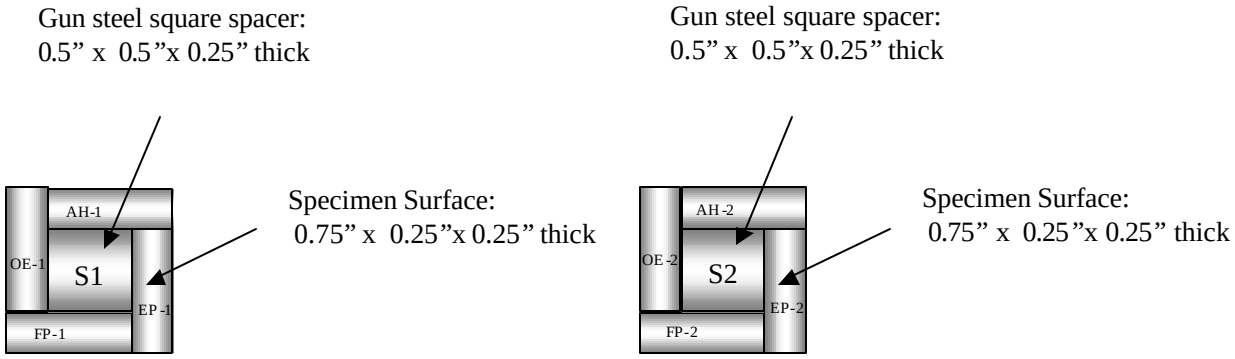

Figure 1. Schematic of specimen arrangement in planar magnetron sputtering system.

Table 1. Surface Finish Measured Via Profilometry

Sample	*RMS Surface Finish (µin.)*
AH-1 (as-honed)	14–16
AH-2 (as-honed)	14–16
EP-1 (electro-polish)	8–10
EP-2 (electro-polish)	9–11
FP-1 (fine polish)	2–4
FP-2 (fine polish)	2–4
OE-1 (oxalic etch)	5–6
OE-2 (oxalic etch)	5–6

PROCEDURE

The following formula for oxalic acid solution was used in these studies: 60 mL H_2O, 2 g oxalic acid, and 4 mL H_2O_2. Two gun steel specimens were completely submerged in the oxalic acid solution. The specimens were first electro-cleaned for 30 seconds in 50 g/L KOH and 25 g/L K_2CO_3 for removal of oils and excess debris. The oxalic acid solution was then heated up to 45°C using a proportional temperature controller, YSI model 72. The steel specimens were immersed into the baths for 10 minutes. After extraction, each specimen was rinsed with warm water and wiped with cotton swabs for removal of a thin layer of dark debris generated from the oxalic etching process. Each specimen was then electro-cleaned for 30 seconds in 50 g/L KOH and 25 g/L K_2CO_3 and finally rinsed with alcohol.

For the comparative study, six more steel specimens were prepared under alternative methods. Two specimens were electro-polished in a 50/50 sulfuric/phosphoric acid solution for 2 minutes at 50°C with 0.75 A of current. The current density, solution concentrations, and bath temperature are comparable to that of the Watervliet Arsenal standard electro-polishing procedure for gun tubes prior to electroplating (ref 1). Each electro-polished specimen was subjected to a warm water rinse and electro-cleaning, as with the oxalic acid etched specimens. An additional two specimens were left in the as-honed 16-µin. finish condition prior to sputtering and the final two specimens were fine polished with SiC polishing paper to a 2- to 4-µin. finish. The RMS surface finish range measured via profilometry of each specimen are given in Table 1.

All specimens were sputtered with 5 µm of α-phase tantalum and subjected to micro-scratch adhesion testing to determine adhesion strength. Micro-scratch adhesion testing is a standard method for testing the adhesion strength of thin films (<15 µm) and is described elsewhere (ref 2). A planar magnetron system with a 2-in. tantalum target was used to deposit the coatings. The base pressure in the system prior to deposition was 6×10^{-7} torr. The target to substrate distance was 2 in. and the sputtering pressure was 10 mtorr Ar gas. The sputtering parameters for the depositions are as follows—1) substrate temperature: 320 ± 10ºC; 2) voltage: 365 ± 5 V; (3) current: 0.950 ± 0.008 A; and (4) power: 350 ± 1 W.

RESULTS

Figures 2a and b represent typical Laser Scanning Confocal Microcopy (LSCM) images of a steel specimen before and after exposure to the oxalic acid solution. After 10 minutes of exposure time, the amount of steel removed from this sample was an estimated 6–8 µm. The etched surface of the steel is similar to that seen in the smooth, etched microstructure of polished cross-sections of the tempered martensite gun steel. Similar images for the electro-polished and fine-polished surfaces are given in Figures 2c and d.

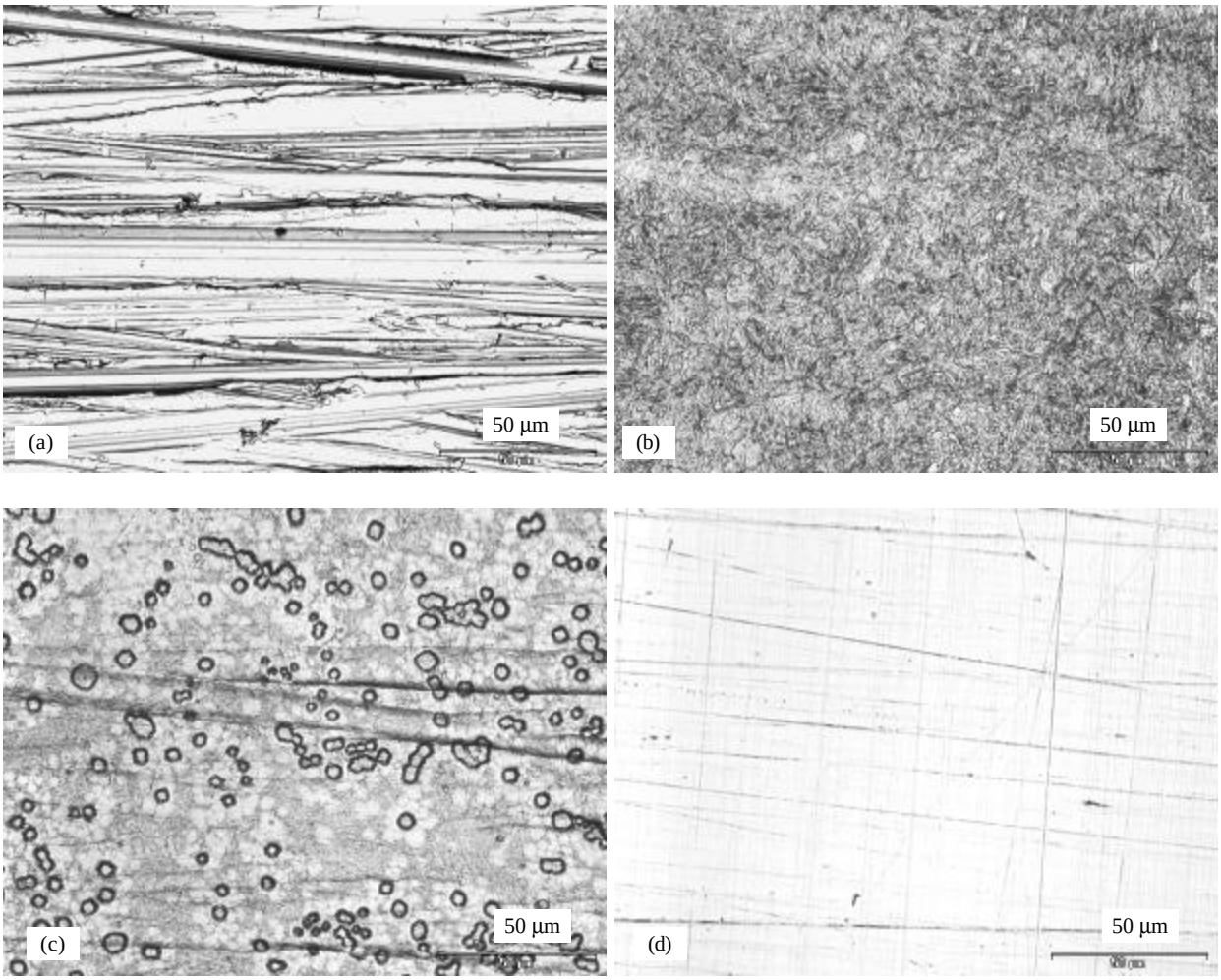

Figure 2. LSCM images of steel specimens: (a) as-honed 16 µin. finish, (b) oxalic etched surface, (c) electro-polished surface, and (d) fine-polished surface.

The weight of the material removed is given in Table 2 for each specimen.

Table 2. Weight Loss of Specimens Upon Etching

Surface Preparation	*Initial Mass (g)*	*Final Mass (g)*	*Mass Removed (g)*
As-polished—16 µin.	–	5.9287	–
As-polished—16 µin.	–	5.9176	–
Electro-polish—50C, 14 A/dm^2—2 min	5.9475	5.9283	0.0192
Electro-polish—50C, 14 A/dm^2—2 min	5.8771	5.8585	0.0186
Fine Polish—2–4 µin.	–	5.7790	–
Fine Polish—2–4 µin.	–	6.0424	–
Oxalic acid dip—45ºC—10 min	5.9090	5.8960	0.0130
Oxalic acid dip—45ºC—10 min	5.9727	5.9531	0.0196

After sputtering, the specimens were re-imaged to see the effects of each surface finish before and after deposition of sputtered tantalum. As is illustrated in Figures 3 and 4, the coating replicates the pre-sputtered surface.

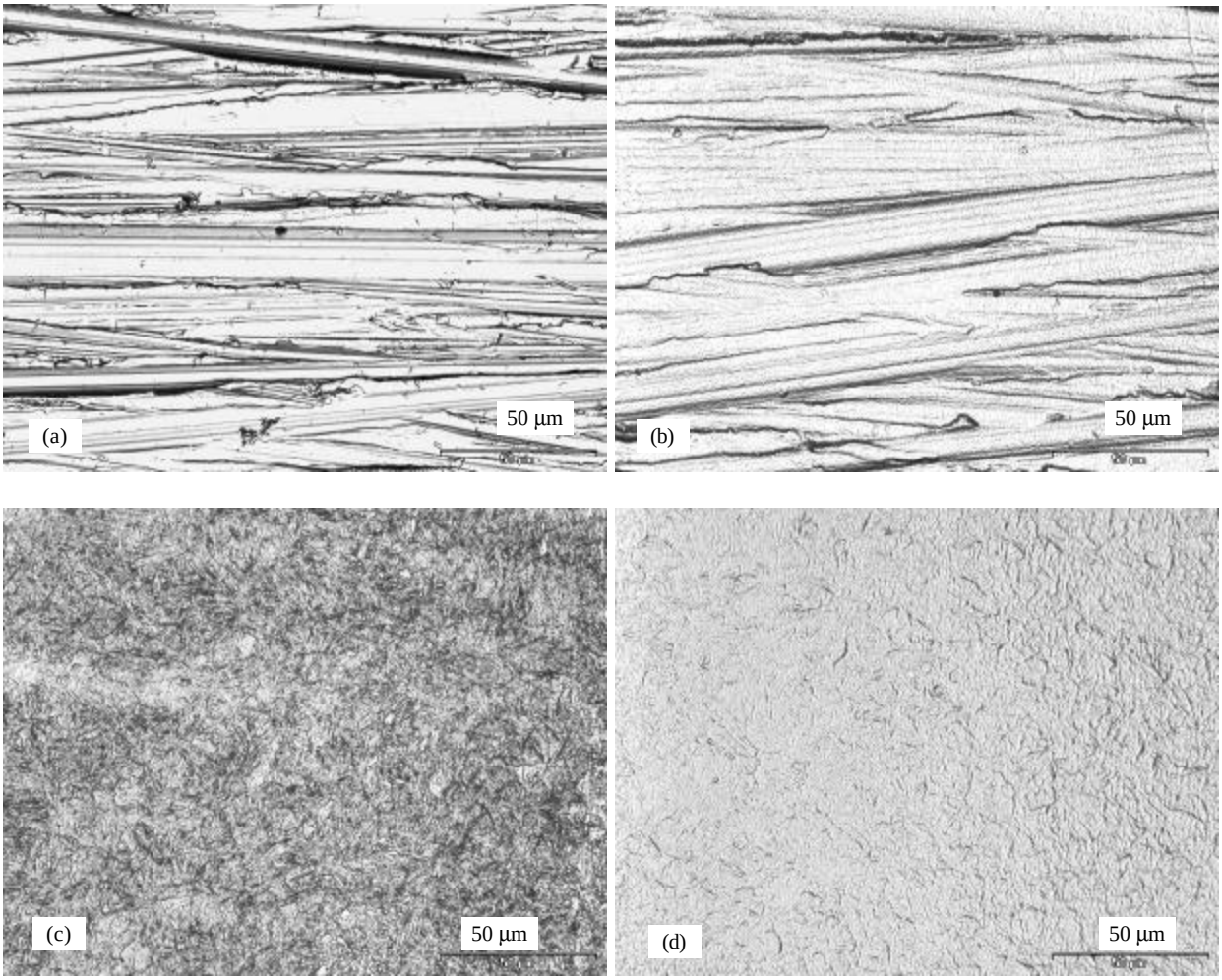

Figure 3. LSCM images of steel specimens before and after sputtering: (a) as-honed 16-µin. finish pre-sputtering, (b) as-honed 16-µin. finish post-sputtering, (c) oxalic etched surface pre-sputtering, and (d) oxalic etched surface post-sputtering.

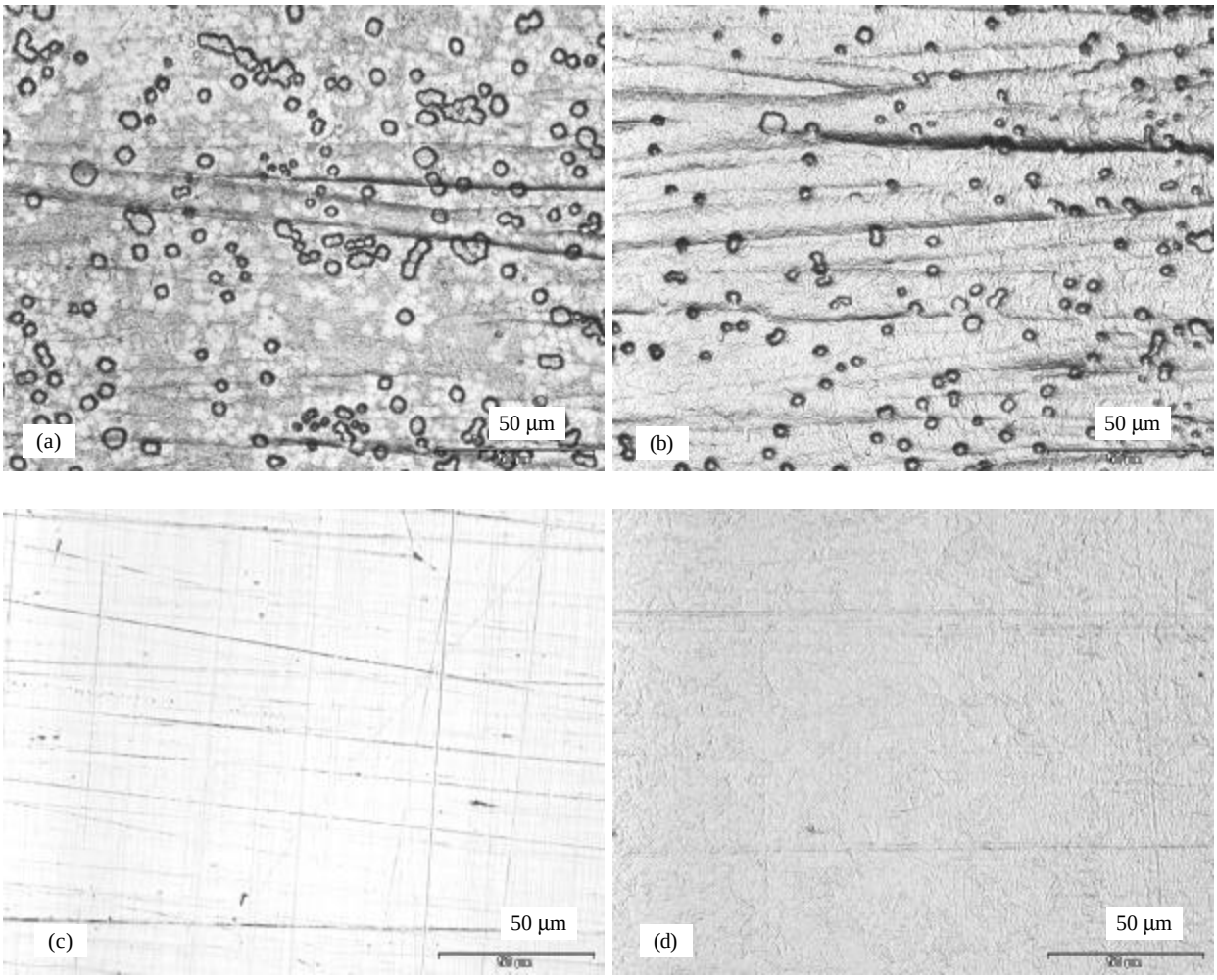

Figure 4. LSCM images of steel specimens before and after sputtering: (a) WVA electro-polish pre-sputtering, (b) WVA electro-polish post-sputtering, (c) fine-polished surface pre-sputtering, and (d) fine-polished surface post-sputtering

The eight 120-mm arc specimens were tested using a CSM Micro-scratch device. Each specimen was scratched three to four times under a progressive load, and an average critical load was measured from readings using acoustic emissions and tangential force recordings that correspond to a coating adhesive failure event, verified by optical microscopy. The results indicated good repeatability of data (within 5%) over each set of specimens. The averaged critical load of the second set of specimens was higher than the first set. This gives evidence that critical load is related to coating thickness, as the thickness of the sputtered coating for the second set of specimens was ~0.5 µm thicker (based on weight gain) than that of the first set. Generally thicker coatings require a greater load to induce coating delamination. Table3 gives the average numbers for critical load of continuous delamination.

Table 3. Critical Loads of Adhesive Failure as Measured by Micro-Scratch Testing

Sample	*Critical Load (N)*
AH-1 (as-honed)	9.74
AH-2 (as-honed)	9.93
EP-1 (electro-polish)	8.17
EP-2 (electro-polish)	8.32
FP-1 (fine polish)	10.40
FP-2 (fine polish)	11.16
OE-1 (oxalic etch)	11.13
OE-2 (oxalic etch)	12.25

These results showed that the electro-polished specimens have a critical load ~15% lower than the as-honed specimens. The fine-polished specimens have a critical load ~10% higher than the as-honed specimens. And the oxalic etch had a critical load ~20% higher than that of the as-honed specimens.

DISCUSSION

The oxalic acid etched specimens performed best in adhesion strength characterization from micro-scratch tests results, outperforming the as-honed, electro-polished, and fine-polished specimens. The surface of the steel (Figure 2) subsequent to honing is very rough and consists of deformed and "folded over" regions. Within these deformed regions near the surface, oils and other contaminants may be present. It is feasible that the likely presence of contaminants is the primary factor in the decrease in adhesion strength when comparing the as-honed steel specimens to the oxalic acid etched and fine-polished specimens. Although sputter cleaning does remove some of the surface material prior to sputtering, results indicate that the complete removal of these contaminants is improbable. An example of this incomplete contamination removal is given in Figure 5. Figure 5a shows the surface of a steel coupon that was polished in oil to a 15-µin. finish, similar to the as-honed surface finish. After sputter cleaning at a level of 5–6 C/cm^2, roughly 2 µm of material is removed. The surface finish was only reduced from 16 to ~11–12 µin. and, as Figure 5b indicates, the contaminants (the image's dark regions) presumed under the "folded over" regions become exposed with the formation of pits.

The adhesion strength performance of the oxalic acid etched surface is comparable to that of the fine-polished surface. The slight increase in average critical load of the oxalic acid etched specimens may be attributable to the existence of microscopic defects in the oxalic acid etched steel surface as illustrated in Figure 2b. During thin film nucleation, a larger density of surface defects provides a larger density of high-energy sites for nucleation that would, in effect, create a more contiguous structure at the coating/substrate interface and increase adhesion strength (ref 3). In addition, the microscopic roughening of the surface induced upon etching may increase the fracture toughness of the interface.

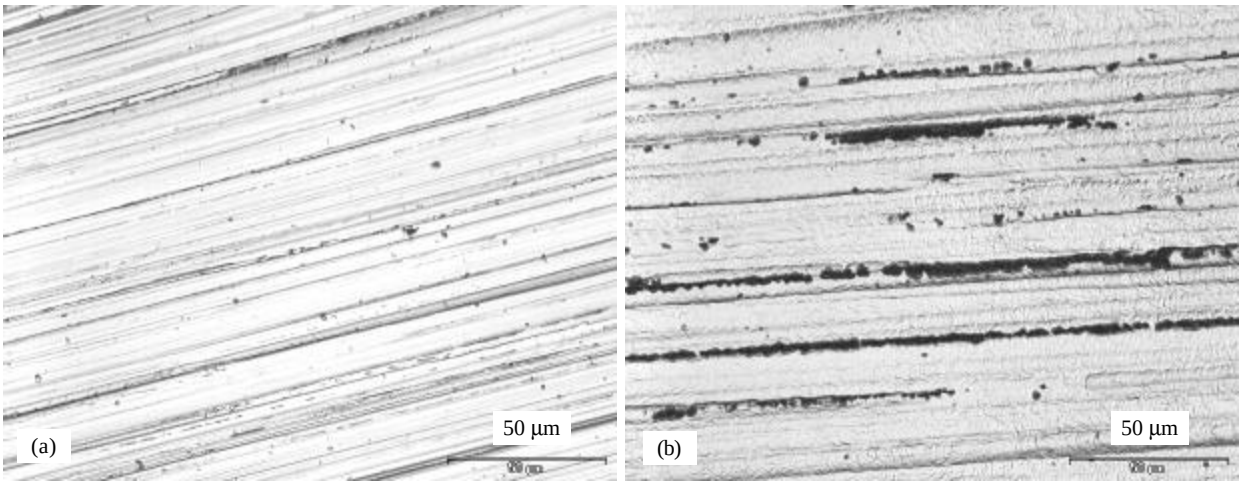

Figure 5. Incomplete contaminant removal: (a) 15-µin. surface, (b) ~11–12 µin. surface after ~2 µm of material was removed via sputter cleaning.

The higher critical loads of the oxalic acid etched surface vs. the electropolished steel surface were unexpected. The oxalic acid etched surfaces and the electro-polished surfaces are different because the nodules introduced by electro-polishing, illustrated in Figures 4a and b, are removed during the reverse plating process (effectively planarizing the surface) in which material is removed from the bore directly prior to the electro-plating of chromium (ref 4). As is illustrated in Figure 4, these nodules were not removed by the sputter cleaning process. The presence of these nodules may act as preferential failure sites in the micro-scratch adhesion test and will yield lower critical loads. Moreover, contaminants at these sites may induce poor adhesion quality of the electro-polished surface.

CONCLUSIONS

Micro-scratch test results suggest that the oxalic acid etching technique is a potential alternative to electro-polishing in the surface pre-treatment of steel prior to sputter deposition.

RECOMMENDATIONS

Other tests, such Laser Pulse Heating (ref 5) may be employed for future research to substantiate the advantages of oxalic acid etching vs. electro-polishing.

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